Multipole as f-Electron Spin-Charge Density in Filled Skutterudites

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It is shown that f-electron multipole is naturally defined as spin-charge one-electron density operator in the second-quantized form with the use of tensor operator on the analogy of multipole expansion of electromagnetic potential from charge distribution in electromagnetism. Due to this definition of multipole, it is possible to determine multipole state from a microscopic viewpoint on the basis of the standard linear response theory for multipole susceptibility. In order to discuss multipole properties of filled skutterudites, we analyze a seven-orbital impurity Anderson model by employing a numerical renormalization group method. We show our results on possible multipole states of filled skutterudite compounds.

KEYWORDS: multipole, spin-charge density, filled skutterudites, numerical renormalization group method

1. Introduction

One of current research trends in material science is to synthesize new compounds which exhibit exotic phenomena concerning magnetism and superconductivity. Due to the improvement of single crystal quality with the use of modern crystal growth techniques, essentially new phenomena have been also discovered even in known compounds. In particular, ordering of higher-rank multipole has been actively studied both from experimental and theoretical sides in the research field of strongly correlated f-electron systems.[1,2] In general, owing to the strong spin-orbit coupling of f electrons, spin-orbital complex degree of freedom, i.e., multipole, is considered to be active in f-electron compounds. However, when orbital degeneracy is lifted, for instance, due to the crystal structure with low symmetry, only spin degree of freedom often remains. Namely, f-electron compounds crystallizing in the cubic structure with high symmetry are quite important for the research of multipole phenomena.

In this sense, filled skutterudite compounds LnT_4X_{12} with lanthanide Ln, transition metal atom T, and pnictogen X provide us an ideal stage for the promotion of multipole physics, since this material group crystallizes in the cubic structure of T_h point group.[3] Moreover, it is possible to synthesize many isostructural materials with different kinds of rare-earth and actinide ions, leading to the development of systematic research on multipole ordering. In fact, recent experiments in cooperation with phenomenological theory have revealed that multipole ordering frequently appears in filled skutterudites. For instance, a rich phase diagram of $PrOs_4Sb_{12}$ with field-induced quadrupole order has been unveiled experimentally and theoretically.[4–6] Recently, antiferro Γ_1-type higher multipole order[1] has been discussed for $PrRu_4P_{12}$[7,8] and $PrFe_4P_{12}$.[9–11] Except for Pr-based filled skutterudites, signs of multipole phenomena have been also found. In $NdFe_4P_{12}$, a significant role of quadrupole at low temperatures has been suggested from the measurement of elastic constant.[12] In $SmRu_4P_{12}$, a possibility of octupole order has been proposed from several kinds of experiments.[13–17]

As mentioned above, theoretical research on multipole order has been developed mainly from a phenomenological viewpoint on the basis of an LS coupling scheme for multi-f-electron state. Such investigations could explain several experimental results and research activity along this direction will be still important in future. However, we strongly believe that it is also important to promote microscopic approach for understanding of multipole phenomena in parallel with phenomenological research. Based on this belief, the present author and collaborators have made effort to develop a microscopic theory for multipole-related phenomena by exploiting a j-j coupling scheme.[18] In particular, octupole ordering in NpO_2 has been clarified by evaluating multipole interaction with the use of the standard perturbation method in terms of electron hopping.[19–21] We have also discussed possible multipole states of filled skutterudites by analyzing multipole susceptibility of a multiorbital Anderson model based on the j-j coupling scheme.[22–27]

However, it seems to be still difficult to understand intuitively the physical meaning of multipole degree of freedom due to the mathematically complicated form of multipole operator defined by using total angular momentum. As mentioned above, multipole is considered to be spin-orbital combined degree of freedom. In this sense, it seems to be natural to regard multipole as anisotropic spin and/or charge density. This point has been first emphasized in the visualization of octupole order in NpO_2.[19–21] The definition of multipole as spin-charge density has been briefly discussed, when we have attempted to clarify multipole state of heavy lanthanide filled skutterudite.[28] Owing to the definition of multipole in the form of one-electron spin-charge density operator, it has been possible to discuss unambiguously multipole state by evaluating multipole susceptibility even for heavy rare-earth compounds with large total angular momentum.

In this paper, first we explain the definition of multipole as spin-charge density in the form of one-body operator from the viewpoint of multipole expansion of electromagnetic potential from charge distribution in electromagnetism. In order to determine the multipole state, we use the optimization of multipole susceptibility on the basis of the standard linear response theory. To proceed with further discussion, in this paper we pick up an impurity Anderson model including seven f orbitals. We perform the calculation of multipole susceptibility by using a numerical renormalization group tech-

nique. Then, we review our recent results of heavy rare-earth filled skutterudites for Ln=Gd∼Yb. We also show our new result for multipole susceptibility of Sm-based filled skutterudites with some comments on the effect of rattling. Finally, we summarize this paper and briefly discuss a future problem of multipole theory. Throughout this paper, we use such units as $\hbar=k_B=1$ and the energy unit is set as eV.

2. Multipole as Spin-Charge Density

In general, multipole is a concept to express the degree of deviation from spherical symmetric structure. A well-known example can be found in the multipole expansion of electromagnetic potential from charge distribution. The potential is formally expanded by the spherical harmonics Y_{LM} and both electric and magnetic multipole moments are defined from the expansion coefficients.

Here we emphasize that the multipole expansion is also applicable for the consideration of electromagnetic field produced by electrons.[29] For instance, Kubo and Kuramoto have discussed the multipole expansion of the vector potential from local electrons, in order to estimate the internal magnetic field from octupole moment in $Ce_xLa_{1-x}B_6$.[30]

Based on the above background, now we consider the definition of multipole as f-electron density operator $\hat{X}$, which is generally expressed in the second-quantized form as

$$\hat{X} = \sum_{m\sigma,m'\sigma'} X_{m\sigma,m'\sigma'} f^{\dagger}_{m\sigma} f_{m'\sigma'}, \tag{1}$$

where $f_{m\sigma}$ is the annihilation operator for f electron with spin σ and z-component m of angular momentum $\ell=3$. Throughout this paper, we define $\sigma=1$ (-1) for up (down) spin. The form of the coefficient $X_{m\sigma,m'\sigma'}$ is related to the definition of multipole. As easily understood, $\hat{X}$ denotes total charge, i.e., monopole, for

$$X^{\text{monopole}}_{m\sigma,m'\sigma'} = \delta_{mm'}\delta_{\sigma\sigma'}. \tag{2}$$

Intuitively, we can understand that f-electron multipole denotes the deviation from the total charge operator. In the standard definition, dipole denotes total angular momentum J. Thus, $\hat{X}$ for dipole is given by

$$X^{\text{dipole}}_{m\sigma,m'\sigma'} = J^{\alpha}_{m\sigma,m'\sigma'} = \delta_{\sigma\sigma'}L^{\alpha}_{mm'} + S^{\alpha}_{\sigma\sigma'}\delta_{mm'}, \tag{3}$$

where α indicates Cartesian component, L denotes angular momentum operator for $\ell=3$ and S indicates spin operator. Then, how do we define higher-order multipoles?

In the multipole expansion of potential in electromagnetism, higher electric and magnetic multipole moments appear in the coefficients of the expansion by the spherical harmonics Y_{LM} with larger angular momentum. In group theory, Y_{LM} is defined by the basis of irreducible representation $D^{(L)}$ of the rotation group R, expressed as

$$RY_{LM} = \sum_{M'} Y_{LM'} D^{(L)}_{MM'}. \tag{4}$$

On the analogy of the multipole expansion, for f-electron multipole operator, we exploit a concept of spherical tensor operator in the quantum mechanics of angular momentum.[31] When we consider the rotation of operator $\hat{T}$, we obtain a set of operators $\hat{T}^{(k)} = \{\hat{T}^{(k)}_q\}$ with $(2k+1)$-components

$(q = -k, -k+1, \cdots, k-1, k)$, given by

$$R\hat{T}^{(k)}_q R^{-1} = \sum_{q'} \hat{T}^{(k)}_{q'} D^{(k)}_{qq'}. \tag{5}$$

Namely, $\hat{T}^{(k)}_q$ is transformed like a basis of irreducible representation $D^{(k)}$ for the rotation. Such $\hat{T}^{(k)}_q$ is called spherical tensor operator of rank k.

The spherical tensor operator $\hat{T}^{(k)}_q$ for f electron is expressed in the second-quantized form as

$$\hat{T}^{(k)}_q = \sum_{m\sigma,m'\sigma'} T^{(k,q)}_{m\sigma,m'\sigma'} f^{\dagger}_{m\sigma} f_{m'\sigma'}, \tag{6}$$

where the coefficient $T^{(k,q)}_{m\sigma,m'\sigma'}$ is calculated as follows. First it is convenient to change the f-electron basis from (m,σ) to (j,μ), where j is the total angular momentum and μ is the z component of j. Note that j takes $7/2$ and $5/2$ for f electrons. For a certain value of angular momentum j and its z-component μ, the matrix element of spherical tensor operator is easily calculated by the Wigner-Eckart theorem as

$$\langle j\mu|T^{(k)}_q|j\mu'\rangle = \frac{\langle j||T^{(k)}||j\rangle}{\sqrt{2j+1}}\langle j\mu|j\mu' kq\rangle, \tag{7}$$

where $\langle JM|J'M'J''M''\rangle$ denotes the Clebsch-Gordan coefficient and $\langle j||T^{(k)}||j\rangle$ is the reduced matrix element for spherical tensor operator, given by

$$\langle j||T^{(k)}||j\rangle = \frac{1}{2^k}\sqrt{\frac{(2j+k+1)!}{(2j-k)!}}. \tag{8}$$

Note that $k \leq 2j$ and the highest rank is $2j$.[32] The coefficient $T^{(k,q)}_{m\sigma,m'\sigma'}$ is obtained by returning to the basis of (m,σ) from (j,μ). The result is given by

$$T^{(k,q)}_{m\sigma,m'\sigma'} = \sum_{j,\mu,\mu'} \frac{\langle j||T^{(k)}||j\rangle}{\sqrt{2j+1}}\langle j\mu|j\mu' kq\rangle$$
$$\times \langle j\mu|\ell m s\frac{\sigma}{2}\rangle\langle j\mu'|\ell m' s\frac{\sigma'}{2}\rangle, \tag{9}$$

where $\ell=3$, $s=1/2$, $j=\ell\pm s$, and μ runs between $-j$ and j.

We note that it is not necessary to take double summations concerning j in eq. (9), since the matrix representation of total angular momentum $\boldsymbol{J}$ is block-diagonalized in the (j,μ)-basis. We have checked that the same results as eq. (9) are obtained when we calculate higher-order multipole operators by following the symmetrized expression of multiple products of J.[31,33,34]

Thus far, we have implicitly assumed f-electron density in an isolated ion, but in actuality, rare-earth ions are in the cubic crystal structure. Then, it is convenient to change from spherical to cubic tensor operators, given by

$$\hat{T}^{(k)}_\gamma = \sum_q G^{(k)}_{\gamma,q}\hat{T}^{(k)}_q, \tag{10}$$

where k is a rank of multipole, an integer q runs between $-k$ and k, γ is a label to express O_h irreducible representation, and $G^{(k)}_{\gamma,q}$ is the transformation matrix between spherical and cubic harmonics. Throughout this paper, we use the cubic tensor operator as multipole.

It should be noted here that multipoles belonging to the same symmetry are mixed in general, even if the rank is different. In addition, multipoles are also mixed due to the effect

of crystalline electric field (CEF) of T_h point group. Namely, the f-electron spin-charge density should be given by the appropriate superposition of multipoles, expressed as

$$\hat{X} = \sum_{k,\gamma} p_\gamma^{(k)} \hat{T}_\gamma^{(k)}. \tag{11}$$

In order to determine the coefficient $p_\gamma^{(k)}$, we evaluate the multipole susceptibility in the linear response theory.[24] Namely, $p_\gamma^{(k)}$ is determined by the normalized eigenstate of susceptibility matrix, defined as

$$\chi_{k\gamma,k'\gamma'} = \frac{1}{Z} \sum_{i,j} \frac{e^{-E_i/T} - e^{-E_j/T}}{E_j - E_i} \langle i|[\hat{T}_\gamma^{(k)} - \rho_\gamma^{(k)}]|j\rangle$$
$$\times \langle j|[\hat{T}_{\gamma'}^{(k')} - \rho_{\gamma'}^{(k')}]|i\rangle, \tag{12}$$

where E_i is the eigenenergy for the i-th eigenstate $|i\rangle$ of the Hamiltonian H of the system, T is a temperature, $\rho_\gamma^{(k)} = \sum_i e^{-E_i/T} \langle i|\hat{T}_\gamma^{(k)}|i\rangle/Z$, and Z is the partition function given by $Z = \sum_i e^{-E_i/T}$.

When we express the multipole moment as eq. (11), we normalize each multipole operator so as to satisfy the orthonormal condition $\text{Tr}\{\hat{T}_\gamma^{(k)} \hat{T}_{\gamma'}^{(k')}\} = \delta_{kk'} \delta_{\gamma\gamma'}$.[35] We note that the multipole susceptibility is given by the eigenvalue of the susceptibility matrix. Note also that the susceptibility for 4u multipole moment does *not* mean magnetic susceptibility, which is evaluated by the response of magnetic moment $\boldsymbol{L}+2\boldsymbol{S}$, i.e., $\boldsymbol{J}+\boldsymbol{S}$.[22,23]

3. Model and Parameters

In the previous section, we have defined multipole as spin-charge density in the form of one-body operator. In order to determine the multipole state, we have explained a method to optimize the multipole susceptibility based on the linear response theory. To proceed with further discussion, it is necessary to set the Hamiltonian H. For f-electron systems, it is desirable to treat a seven-orbital periodic Anderson model, but at least at present, it seems to be a heavy task to analyze such a multiorbital model. To reduce the task in calculations by keeping essential physics, we can take two ways.

One is to decrease the number of relevant f orbitals in the periodic system. As for the research along this line, here we briefly introduce the theoretical study on octupole order in NpO_2.[19–21] After the discussion about the CEF states of actinide dioxides, two relevant Γ_8 orbitals have been extracted. Then, on the basis of a j-j coupling scheme, the Γ_8 orbital degenerate Hubbard model has been set as an effective Hamiltonian for NpO_2. With the use of the standard perturbation theory in terms of f-electron hopping, effective interactions between multipoles in adjacent sites have been evaluated on an fcc lattice. Due to the combination of exact diagonalization and mean-field theory, it has been concluded that the ground state has longitudinal triple-$\boldsymbol{q}$ 5u octupole order, consistent with experimental facts.

Another way is to keep all seven f orbitals, but to consider an impurity Anderson model. Even if the number of local degree of freedom is increased, it is possible to solve the impurity Anderson model with the use of a numerical renormalization group method. In this paper, we adopt this way to discuss multipole state of filled skutterudites.

The seven-orbital Anderson model for filled skutterudites is given by

$$H = \sum_{\boldsymbol{k},\sigma} \varepsilon_{\boldsymbol{k}} c_{\boldsymbol{k}\sigma}^\dagger c_{\boldsymbol{k}\sigma} + \sum_{\boldsymbol{k},\sigma,m} (V_m c_{\boldsymbol{k}\sigma}^\dagger f_{m\sigma} + \text{h.c.}) + H_{\text{loc}}, \tag{13}$$

where $\varepsilon_{\boldsymbol{k}}$ is conduction electron dispersion and $c_{\boldsymbol{k}\sigma}$ is the annihilation operator for conduction electron with momentum $\boldsymbol{k}$ and spin σ. The second term indicates the hybridization between conduction and f electrons. For filled skutterudites, the main conduction band is given by a_u, constructed from p-orbitals of pnictogen.[36] Note that the hybridization occurs between the states with the same symmetry. Since the a_u conduction band has xyz symmetry, we set $V_2 = -V_{-2} = V$ and zero for other m. We fix V as $V = 0.05$ eV and a half of the bandwidth of a_u conduction band is set as 1 eV.

The third term in H is the local f-electron part, given by

$$H_{\text{loc}} = H_{\text{so}} + H_{\text{int}} + H_{\text{CEF}}. \tag{14}$$

Note that the chemical potential is appropriately changed to adjust the local f-electron number n. The spin-orbit coupling term H_{so} is given by

$$H_{\text{so}} = \lambda \sum_{m,\sigma,m',\sigma'} \zeta_{m,\sigma,m',\sigma'} f_{m\sigma}^\dagger f_{m'\sigma'}, \tag{15}$$

where λ is the spin-orbit coupling and $f_{m\sigma}$ denotes the annihilation operator for f electron with spin σ and angular momentum $m (=-3,\cdots,3)$ and $\sigma=+1$ (-1) for up (down) spin. The matrix elements are expressed by $\zeta_{m,\pm1,m,\pm1} = \pm m/2$, $\zeta_{m\pm1,\mp1,m,\pm1} = \sqrt{12 - m(m\pm1)}/2$, and zero for the other cases. The second term H_{int} indicates the Coulomb interactions among f electrons, expressed by

$$H_{\text{int}} = \sum_{\substack{m_1 \sim m_4 \\ \sigma_1,\sigma_2}} I_{m_1,m_2,m_3,m_4} f_{m_1\sigma_1}^\dagger f_{m_2\sigma_2}^\dagger f_{m_3\sigma_2} f_{m_4\sigma_1}, \tag{16}$$

where the Coulomb integral I is expressed by the combination of Slater-Condon parameters, F^0, F^2, F^4, and F^6.[37]

Finally, the CEF term H_{CEF} is given by

$$H_{\text{CEF}} = \sum_{m,m',\sigma} B_{m,m'} f_{m\sigma}^\dagger f_{m'\sigma}, \tag{17}$$

where $B_{m,m'}$ is determined from the table of Hutchings for angular momentum $J=\ell=3$,[38] since we are now considering the potential for f electron. For filled skutterudites with T_h symmetry,[3] $B_{m,m'}$ is expressed by using three CEF parameters B_4^0, B_6^0, and B_6^2.[38] Following the traditional notation, we define

$$B_4^0 = Wx/F(4),$$
$$B_6^0 = W(1-|x|)/F(6), \tag{18}$$
$$B_6^2 = Wy/F^t(6),$$

where x and y specify the CEF scheme for T_h point group,[3] while W determines an energy scale for the CEF potential. Concerning $F(4)$, $F(6)$, and $F^t(6)$, we choose $F(4)=15$, $F(6)=180$, and $F^t(6)=24$ for $\ell=3$.[38,39]

For further discussions, it is necessary to set the parameters. First let us consider the Slater-Condon parameters F^k ($k=0, 2, 4,$ and 6) and spin-orbit coupling λ. We will discuss CEF parameters later. In order to determine F^k and λ, we try to reproduce the f^2 excitation spectrum of Pr^{3+} ion.[40,41] Here we consider twelve excited states, which are labeled as $^3H_5$, $^3H_6$, $^3F_2$, $^3F_3$, $^3F_4$, $^1G_4$, $^1D_2$, $^3P_0$, $^3P_1$, $^3P_2$, $^1I_6$, and
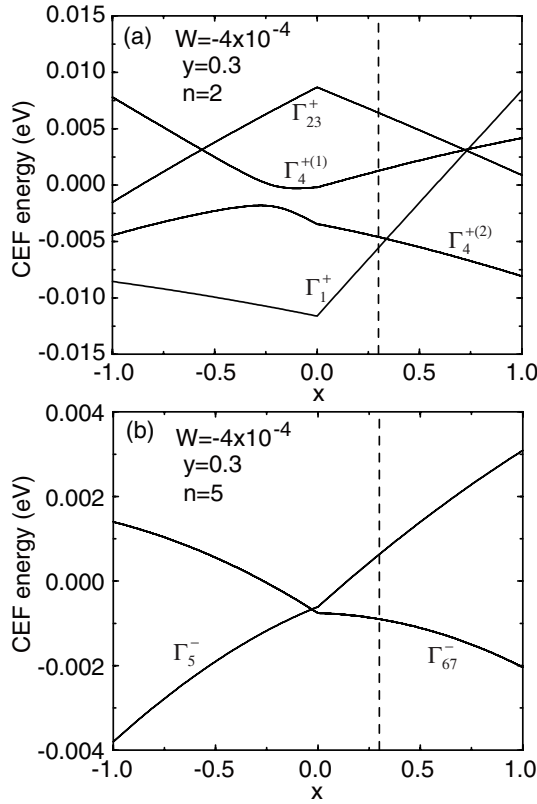
Fig. 1.   CEF energy levels for (a) $n=2$ and (b) $n=5$.
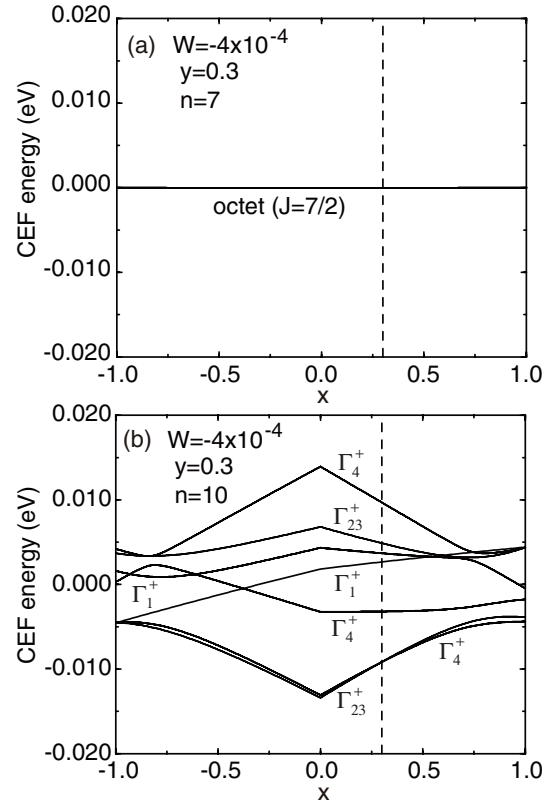
Fig. 2.   CEF energy levels for (a) $n=7$ and (b) $n=10$.

$^1S_0$. By diagonalizing $H_{\text{so}} + H_{\text{int}}$, we obtain eigenenergies E_j and define excitation energy $\delta E_j = E_j - E_0$, where E_0 is the ground state energy for $^3H_4$. We determine F^k and λ so as to minimize the sum of the square of energy difference, given by $\Delta = \sum_{j=1}^{12}(\delta E_j^{\text{exp}} - \delta E_j)^2$, where δE_j^{exp} indicates the excitation energy experimentally determined. Note that F^0 cannot be determined in the present simple procedure, since it appears only as the offset of the energy level when local f-electron number is assumed to be unchanged. In order to determine the value of F^0 itself, it is necessary to resort to the first-principle calculation, but it is out of the scope of this paper. Here we simply set by hand $F^0=10$ eV as a typical value for rare-earth ion.

After the minimization of Δ, we obtain $F^2=8.75$ eV, $F^4=6.60$ eV, $F^6=4.44$ eV, and $\lambda=0.095$ eV. These values are expected to be reasonable, since the experimental value of λ is 0.094 eV. For other lanthanides, we use the same values for the Slater-Condon parameters, since there is no reason to change two-body interactions, even when the electron number is changed. On the other hand, since the spin-orbit interaction is considered to be sensitive to ion radius, we use experimental values of λ for each lanthanide such as $\lambda=0.144$ eV (Sm), 0.180 eV (Gd), 0.212 eV (Tb), 0.240 eV (Dy), 0.265 eV (Ho), 0.295 eV (Er), 0.326 eV (Tm), and 0.356 eV (Yb).[42]

Concerning CEF parameters, we emphasize that electrostatic potentials act on one f-electron state. In principle, it is not necessary to change the CEF parameters when we substitute rare-earth ion, as long as we consider the same crystal structure. Namely, it is enough to determine the CEF parameters for some filled skutterudite compound. First we set $W=-0.4$ meV and $y=0.3$, which are considered to be typical values for filled skutterudites. However, the CEF state is drastically changed by x. From the CEF energy level for $n=2$, as shown in Fig. 1(a), we choose $x=0.3$ so as to reproduce quasi-quartet CEF scheme of $PrOs_4Sb_{12}$.[43–45] We use such CEF parameters for other rare-earth ions. Since we discuss multipole states for Sm-, Gd-, and Ho-based filled skutterudites, here we show the CEF energy schemes for $n=5$, 7, and 10. Results for other cases are found in Ref. 23, although we used different parameters there. Namely, the CEF energy schemes are not changed drastically, as long as we use realistic values for Coulomb interaction and spin-orbit coupling.

In Fig. 1(b), we show the CEF energy levels for $n=5$. There appear Γ_5^- doublet and Γ_{67}^- quartet states for $x < 0$ and $x > 0$, respectively. At $x=0.3$, we obtain Γ_{67}^- quartet ground state. From the specific heat measurements for $SmRu_4P_{12}$ and $SmOs_4P_{12}$, the CEF ground state has been concluded to be Γ_{67}^- quartet.[46] Recently, magnetization measurement has been performed and the observed anisotropy has confirmed the Γ_{67}^- quartet ground state in $SmOs_4Sb_{12}$.[47] On the other hand, the CEF energy scheme can be changed even among the same Sm-based filled skutterudites. In fact, for $SmFe_4P_{12}$, Γ_5^- doublet ground state has been suggested.[46,48] We have explained that such conversion of the CEF ground state at $n=5$ occurs due to the balance between Coulomb interaction and spin-orbit coupling.[27]

In Figs. 2(a) and 2(b), we show the results for $n=7$ and 10, respectively. For the case of Gd^{3+} with $n=7$, the CEF ground state is well described by $L=0$ and $J=S=7/2$, but it is almost independent of x, since the CEF potentials for $L=0$ provide only the energy shift. Note, however, that the CEF state is given by the mixture of the LS and j-j coupling schemes.

This point will be discussed later again. For the case of Ho^{3+} with $n=10$, a remarkable point is that Γ_{23}^+ doublet and Γ_4^+ triplet states are almost degenerate in the wide range of the values of x. In particular, around at $x=0.3$, the ground state is easily converted. Thus, it is necessary to discuss carefully the case of $n=10$.

4. Numerical Results

In order to evaluate the susceptibility matrix, we employ a numerical renormalization group (NRG) method,[49] in which momentum space is logarithmically discretized to include efficiently the conduction electrons near the Fermi energy. In actual calculations, we introduce a cut-off Λ for the logarithmic discretization of the conduction band. Due to the limitation of computer resources, we keep M low-energy states. In this paper, we set $\Lambda=5$ and $M=4500$. Note that the temperature T is defined as $T=\Lambda^{-(N-1)/2}$ in the NRG calculation, where N is the number of the renormalization step.

First let us summarize our recent results for multipole state of heavy lanthanide filled skutterudites.[28] For Ln=Gd, we have found the effect of quadrupole moments due to the deviation from the LS coupling scheme. For Ln=Ho, when the CEF ground state is Γ_{23}^+ doublet, the exotic state dominated by 2u octupole moment has been observed. For Ln=Tb and Tm, the CEF ground state is Γ_1^+ singlet and we have found no significant multipole moments at low temperatures, although we cannot exclude a possibility of antiferro 1g+2g ordering. For Ln=Dy, Er, and Yb, the CEF ground state is Γ_5^- doublet, and the dominant moment is the mixture of 4u and 5u. Among these cases, we pick up the results of Ln=Gd and Ho, and review interesting possibilities for the multipole states.

For the case of Gd^{3+} ion, the dominant multipole component is 4u dipole and the secondary components are 3g and 5g quadrupoles. Note that after the partial screening due to conduction electrons at extremely low temperatures, quadrupole moments disappear, but it seems to observe significant contribution from quadrupole moments. In the LS coupling scheme, the f^7 state is specified by $J=S=7/2$ and $L=0$. Namely, at the first glance, we do not expect the appearance of quadrupole moment. However, we should note that actual situation is always between the LS and j-j coupling schemes. Namely, some finite contribution of the j-j coupling scheme is included in the ground state. If very large λ is assumed, first $j=5/2$ sextet is fully occupied and then, one f electron is accommodated in $j=7/2$ octet. Thus, this state can be multipole-active. Recently, it has been observed in $GdRu_4P_{12}$ that ^{101}Ru NQR frequency exhibits temperature dependence below a Néel temperature $T_N=22K$.[50] This may be interpreted as the effect of quadrupole due to the deviation from the LS coupling scheme.

For the case of Ho^{3+} ion, the CEF ground state is Γ_4^+ triplet at $x=0.3$, but the first excited state is Γ_{23}^+ doublet with very small excitation energy such as 10^{-5} eV. Thus, as shown in Fig. 2(b), Ho-based filled skutterudite is considered to be in the quasi-quintet situation.[23,51] For $x=0.3$, we have found several kinds of multipoles, but the dominant one is always given by the mixture of 4u and 5u from dipole, octupole, dotriacontapole, and octacosahectapole.

Here we note that the CEF ground state is fragile for $n=10$. If we slightly decrease x, the ground state is easily changed. Then, we have evaluated multipole susceptibility for $x=0.25$
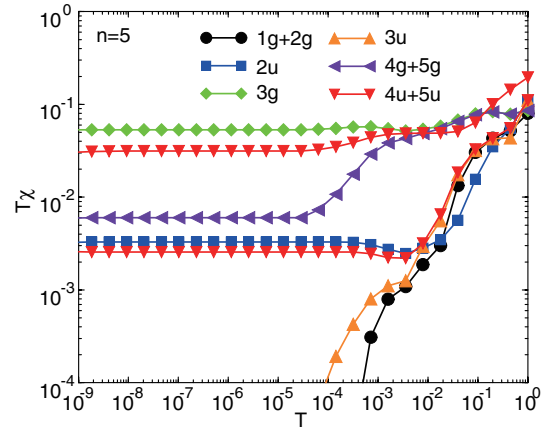

Fig. 3. (Color online) Multipole susceptibility for $n=5$.

with Γ_{23}^+ doublet ground state. The multipole states at high temperatures are similar to those for $x=0.3$, but at low temperatures, we have found 2u multipole state, expressed as $p_{2u}^{(3)}=0.955$ and $p_{2u}^{(7)}=0.297$. Namely, the main component is 2u octupole, but there is contribution of 2u octacosahectapole. From the elastic constant measurement for $HoFe_4P_{12}$, some anomalous features have been discussed.[51] It seems interesting to reexamine experimental results from the viewpoint of 2u octupole state.

Now we show our new result for the case of $n=5$, corresponding to Sm-based filled skutterudites. As mentioned in the introduction part, $SmRu_4P_{12}$ has attracted much attention from a possibility of octupole ordering. It is meaningful to discuss possible multipole state in the present calculation. As shown in Fig. 3, we find that 3g quadrupole is dominant with $p_{3g}^{(2)}=0.995$ and $p_{3g}^{(4)}=0.097$. The secondary component is expressed as 4u+5u, but the contribution from 5u is found to be less than one percent. Note that 4u and 5u are mixed due to the T_h symmetry, although such mixing can be included neither in the LS nor j-j coupling scheme. It is an advantage of the present calculation to take into account the 4u-5u mixing correctly. The third and fourth components are, respectively, expressed by 4g+5g and 2u. The fifth component is also expressed by 4u+5u, which includes significant contribution from 5u octupole.

It is difficult to conclude the ordering of multipole only from the present results, but the local multipole moment with significant weight is considered to be a candidate which is ordered in actual system. Then, if we discuss relevant octupole moment within the present result of the electronic model, 4u octupole seems to be the best candidate, since the secondary component includes 4u octupole moment and the contribution of 5u octupole is very small.

Throughout this paper, we have not included the effect of phonons, but in the filled skutterudite structure, anharmonic local phonon, i.e., rattling, has been considered to play some roles to determine electronic properties. When we have considered that the dominant phonon mode in filled skutterudites is Jahn-Teller type with E_g symmetry,[52] the multipole state for the case of $n=5$ has been found to be characterized by the mixture of 4u magnetic and 5u octupole moments with clear difference between longitudinal and transverse modes.[53] If such symmetry lowering can be detected in experiments,

we should consider seriously the possibility of 5u octupole. We believe that it is an important test of 5u octupole ordering scenario for the Sm-based filled skutterudite.

5.   Summary and Comment

In summary, we have defined the multipole as spin-charge one-electron density operator by using the cubic tensor operator. Based on the linear response theory, we have determined the multipole state so as to maximize the multipole susceptibility. Then, we have discussed possible multipole state of filled skutterudites by evaluating the multipole susceptibility of the seven orbital Anderson model with the use of NRG method. After the review of the results for Ln=Gd~Yb, we have shown the result for Sm-based filled skutterudites. Within the impurity Anderson model, quadrupole moment has been found to be dominant. We have observed that the secondary component is magnetic with significant contribution of 4u octupole. Thus, when we simply ignore the effect of rattling, 4u octupole seems to be relevant in the Sm-based filled skutterudite. It is consistent with recent result on the specific heat measurement of $SmRu_4P_{12}$.[17]

Finally, we briefly comment on the multipole expansion of f-electron spin-charge density. In this paper, the spin-charge density has been expressed by the linear combination of cubic tensor operators in the cubic crystal structure. Unfortunately, it does not provide the general multipole expansion of f-electron spin-charge density, since we are restricted only in the cubic symmetry. It is one of future issues to complete the multipole expansion of f-electron spin-charge density.

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